Claims

[1] A process for producing a metallized ceramic shaped article, comprising: a heating step of heating a non-oxide ceramic shaped article to a temperature at or above a temperature, which is 300°C below the oxidation start temperature of the non-oxide ceramics, without substantial dissolution of oxygen in a solid solution form during heating; an oxidation step of bringing the non-oxide ceramic shaped article heated in the heating step into contact with an oxidizing gas and then holding the non-oxide ceramic shaped article at a temperature above the oxidation start temperature of the non-oxide ceramics to oxidize the surface of the non-oxide ceramic shaped article and thus to form an oxide layer on the surface of the non-oxide ceramic shaped article; and a metallization step of forming a metal layer on the surface of the oxide layer in the non-oxide ceramic shaped article having an oxide layer on its surface produced in the oxidation step.

[2] The method according to claim 1, wherein the heating step comprises the steps of:

(I) introducing the non-oxide ceramic shaped article into a furnace, then discharging an oxidizing substance adsorbed or sorbed to the non-oxide ceramic shaped article and to a furnace material outside of the furnace, so as to regulate

an oxidizing gas content in the atmosphere within the furnace to be not more than 0.5 mmol in terms of total number of moles of the oxidizing gas per m^3 of the inside of the furnace; and

(II) heating the non-oxide ceramic shaped article to a temperature at or above a temperature, which is 300°C below the oxidation start temperature of the non-oxide ceramics, while maintaining the atmosphere in the furnace having an oxidizing gas content of not more than 0.5 mmol in terms of total number of moles of the oxidizing gas per m^3 of the inside of the furnace; and wherein

when bringing the non-oxide ceramic shaped article into contact with the oxidizing gas in the oxidation step, until at least 2 min. elapses after the arrival of the temperature of the non-oxide ceramic shaped article at or above the oxidation start temperature thereof, the pressure or partial pressure of the oxidizing gas is maintained at not more than 50 kPa.

[3] The process according to claim 1 or 2, wherein the metallization step comprises plating treatment.

[4] A metallized ceramic shaped article produced by the method of any one of claims 1 to 3.

[5] A metallized ceramic shaped article comprising: a ceramic shaped article comprising a non-oxide ceramic shaped article composed mainly of a nitride or carbide of a metal or

semimetal and an oxide layer formed of an oxide of an element identical to the metal or semimetal element provided on the surface of the non-oxide ceramic shaped article; and a metal layer provided on the oxide layer, wherein, when a branched crack is divided into a crack unit located between adjacent branch points and crack units extending from the crack end to the nearest branch point, a branched crack having a crack unit simultaneously meeting a "w" value of not less than 20 nm, an "l" value of not less than 500 nm and a "w/l" value of not less than 0.02, wherein "l" (nm) represents the length of each crack unit, and "w" (nm) represents the maximum width of each crack unit, is substantially absent on the surface of the oxide layer.

[6] A metallized ceramic shaped article comprising: a ceramic shaped article comprising a non-oxide ceramic shaped article composed mainly of a nitride or carbide of a metal or semimetal and a 0.1 to 100 μm-thick oxide layer formed of an oxide of an element identical to the metal or semimetal element provided on the surface of the non-oxide ceramic shaped article; and a metal layer provided on the oxide layer, wherein voids are substantially absent in the oxide layer in its region in a thickness of at least 20 nm from the boundary of the non-oxide ceramic layer and the oxide layer.

[7] A Peltier element comprising: a pair of ceramic substrates each having a conductor pattern on its surface and

disposed so as to face each other; a thermoelectric material part comprising P-type thermoelectric materials and N-type thermoelectric materials arranged alternately between the pair of ceramic substrates; an electrode disposed between the thermoelectric material part and one of the ceramic substrates; and an electrode disposed between the thermoelectric material part and the other ceramic substrate, said electrodes being disposed so that the P-type thermoelectric materials and N-type thermoelectric materials constituting the thermoelectric material part are alternately connected electrically, said electrodes being each connected electrically to the conductor pattern in the adjacent ceramic substrate, wherein

the ceramic substrate comprises: a non-oxide ceramic substrate composed mainly of a nitride or carbide of a metal or semimetal and an oxide layer formed of an oxide of an element identical to the metal or semimetal element provided on the surface of the non-oxide ceramic substrate, and, when a branched crack is divided into a crack unit located between adjacent branch points and crack units extending from the crack end to the nearest branch point, a branched crack having a crack unit simultaneously meeting a "w" value of not less than 20 nm, an "l" value of not less than 500 nm and a "w/l" value of not less than 0.02, wherein "l" (nm) represents the length of

each crack unit, and "w" (nm) represents the maximum width of each crack unit, is substantially absent on the surface of the oxide layer.

[8] A Peltier element comprising: a pair of ceramic substrates each having a conductor pattern on its surface and disposed so as to face each other; a thermoelectric material part comprising P-type thermoelectric materials and N-type thermoelectric materials arranged alternately between the pair of ceramic substrates; an electrode interposed between the thermoelectric material part and one of the ceramic substrates; and an electrode interposed between the thermoelectric material part and the other ceramic substrate, said electrodes being disposed so that the P-type thermoelectric materials and N-type thermoelectric materials constituting the thermoelectric material part are alternately connected electrically, said electrodes being each connected electrically to the conductor pattern in the adjacent ceramic substrate, wherein

the ceramic substrate comprises: a ceramic substrate comprising a non-oxide ceramic substrate composed mainly of a nitride or carbide of a metal or semimetal; and a 0.1 to 100 μm-thick oxide layer formed of an oxide of an element identical to the metal or semimetal element provided on the surface of the non-oxide ceramic substrate, and voids are substantially

absent in the oxide layer in its region in a thickness of at least 20 nm from the boundary of the non-oxide ceramic layer and the oxide layer.

[9] A process for producing a Peltier element, said Peltier element comprising: a pair of ceramic substrates each having a conductor pattern on its surface and disposed so as to face each other; a thermoelectric material part comprising P-type thermoelectric materials and N-type thermoelectric materials arranged alternately between the pair of ceramic substrates; an electrode interposed between the thermoelectric material part and one of the ceramic substrates; and an electrode interposed between the thermoelectric material part and the other ceramic substrate, the electrodes being disposed so that the P-type thermoelectric materials and N-type thermoelectric materials constituting the thermoelectric material part are alternately connected electrically, the electrodes being each connected electrically to the conductor pattern in the adjacent ceramic substrate, said process comprising the following steps A, B, and C,

step A: a step of providing a thermoelectric material member comprising alternately arranged P-type thermoelectric materials and N-type thermoelectric materials, wherein the top face of each of the thermoelectric materials is connected

electrically to the top face of the thermoelectric material adjacent to one side thereof through an electrode, and, at the same time, the bottom face of each of the thermoelectric materials is connected electrically to the bottom face of the thermoelectric material adjacent to the other side thereof through an electrode,

step B: a step of providing a pair of ceramic substrates each having a conductor pattern on its surface, the conductor pattern in each of the ceramic substrates being provided so that, when the thermoelectric material member is held between the ceramic substrates, the conductor pattern is connected electrically to the electrode in the thermoelectric material member, and

step C: a step of disposing the thermoelectric material member between the pair of ceramic substrates and soldering the electrodes in the thermoelectric material member to the conductor pattern in each of the ceramic substrates, wherein

said process further comprising the following steps for the production of the ceramic substrates having a conductor pattern on the surface thereof,

step D: a heating step of heating a non-oxide ceramic substrate to a temperature at or above a temperature, which is 300°C below the oxidation start temperature of the non-oxide ceramics, without substantial dissolution of oxygen in a solid

solution form during heating;

step E: an oxidation step of bringing the non-oxide ceramic substrate heated in the step D into contact with an oxidizing gas and then holding the non-oxide ceramic substrate at a temperature above the oxidation start temperature of the non-oxide ceramics to oxidize the surface of the non-oxide ceramic substrate and thus to form an oxide layer on the surface of the non-oxide ceramic substrate; and

step F: a step of forming a pattern of copper or a metal layer composed mainly of copper on the oxide layer in the non-oxide ceramic substrate having an oxide layer on its surface produced in the step E by a thick-film forming method and then forming a layer of a metal different from the metal constituting the metal layer by a plating method onto the pattern.

[10] A Peltier element comprising: a pair of ceramic substrates each having a conductor pattern on its surface and disposed so as to face each other; a thermoelectric material part comprising P-type thermoelectric materials and N-type thermoelectric materials arranged alternately between the pair of ceramic substrates; an electrode disposed between the thermoelectric material part and one of the ceramic substrates; and an electrode disposed between the thermoelectric material part and the other ceramic substrate,

said first and second electrodes being disposed so that the P-type thermoelectric materials and N-type thermoelectric materials constituting the thermoelectric material part are alternately connected electrically, said electrodes being each connected electrically to the conductor pattern in the adjacent ceramic substrate, wherein

the ceramic substrate is "a non-oxide ceramic substrate having an oxide layer on its surface" produced by a process comprising the following steps D and E,

step D: a heating step of heating a non-oxide ceramic substrate to a temperature at or above a temperature, which is 300°C below the oxidation start temperature of the non-oxide ceramics, without substantial dissolution of oxygen in a solid solution form during heating; and

step E: an oxidation step of bringing the non-oxide ceramic substrate heated in the step D into contact with an oxidizing gas and then holding the non-oxide ceramic substrate at a temperature above the oxidation start temperature of the non-oxide ceramics to oxidize the surface of the non-oxide ceramic substrate and thus to form an oxide layer on the surface of the non-oxide ceramic substrate.

[11] The Peltier element according to claim 10, wherein the step D comprises the steps of:

(I) introducing the non-oxide ceramic shaped article

into a furnace, then discharging an oxidizing substance adsorbed or sorbed to the non-oxide ceramic substrate and to a furnace material outside of the furnace, so as to regulate an oxidizing gas content in the atmosphere within the furnace to be not more than 0.5 mmol in terms of total number of moles of the oxidizing gas per m^3 of the inside of the furnace; and

(II) heating the non-oxide ceramic substrate to a temperature at or above a temperature, which is 300°C below the oxidation start temperature of the non-oxide ceramics, while maintaining the atmosphere in the furnace having an oxidizing gas content of not more than 0.5 mmol in terms of total number of moles of the oxidizing gas per m^3 of the inside of the furnace; and

when bringing the non-oxide ceramic substrate into contact with the oxidizing gas in the oxidation step E, until at least 2 min. elapses after the arrival of the temperature of the non-oxide ceramic shaped article at or above the oxidation start temperature thereof, the pressure or partial pressure of the oxidizing gas is maintained at not more than 50 kPa.